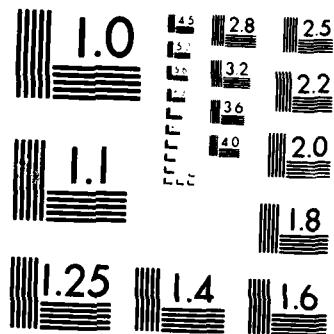END

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Intramolecular Electron Transfer at Metal Surfaces. V.

Pendant Substituent Effects Upon Thiocarboxylate-Bridged

Cobalt(III) Reduction Kinetics at Mercury and Gold Electrodes.

by

Tomi T-T. Li and Michael J. Weaver

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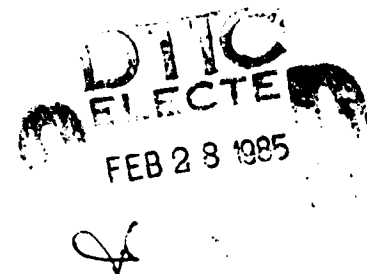Journal of Electroanalytical Chemistry

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slightly larger variations occur in the stability of the precursor
(adsorbed reactant) state at mercury electrodes that are apparently due
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INTRAMOLECULAR ELECTRON TRANSFER AT METAL SURFACES.   V.

PENDANT SUBSTITUENT EFFECTS UPON THIOCARBOXYLATE-BRIDGED

COBALT(III) REDUCTION KINETICS AT MERCURY AND GOLD ELECTRODES.

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ABSTRACT

Unimolecular rate constants, k_{et} (sec^{-1}), are reported for the reduction of pentaamminecobalt(III) anchored to mercury or gold electrodes via thiocarboxylate bridging ligands having the general form $RSCH_2COO^-$. Since the carboxylate is bound to Co(III) and sulfur provides the surface binding group, the substituent R (where R is various alkyl, carboxylate, ketone, or aromatic groups) will be pendant to the thiocarboxylate bridge linking the surface and cobalt reacting centers. Alteration of the pendant group R yields only small (ca. up to 4 fold) variations in k_{et} at a given electrode potential, although slightly larger variations occur in the stability of the precursor (adsorbed reactant) state at mercury electrodes that are apparently due to specific interactions between R and the metal surface.. The insensitivity of k_{et} to the pendant group. is compared and contrasted with the effects of varying the substituent that bridges the redox center to the metal surface. Comparisons are also made with pendant group effects for related redox processes in homogeneous solution.

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We have recently been examining the reduction kinetics of carboxylato-pentaamminecobalt(III) complexes anchored to metal surfaces via a variety of organic thio substituents.[1-5] These reactants are sufficiently strongly adsorbed so to enable unimolecular rate constants for the elementary electron-transfer step, k_{et} (sec^{-1}), to be obtained directly using rapid linear sweep voltammetry.[1] Such processes can be perceived as involving "surface intramolecular" electron transfer since they constitute the heterogeneous analogs of intramolecular reactions involving binuclear metal complexes in homogeneous solution. Measurements of k_{et} along with the corresponding frequency factors obtained from the temperature dependence of k_{et}[5] have enabled detailed assessments to be made of the role of the organic surface anchor in mediating heterogeneous electron transfer. In particular, the degree of electronic coupling between the surface and Co(III), as described by the electronic transmission coefficient κ_{el}, appears to be strongly dependent on the nature of the bridging group. Thus typically $\kappa_{el} \sim 1$ for organic ligands featuring uninterrupted double bond conjugation (i.e., reaction adiabaticity is approached), whereas k_{et} for nonconjugated ligands can be substantially (up to ca. 10^4 fold) smaller apparently from $\kappa_{el} \ll 1$; i.e., as a result of nonadiabatic pathways.[1-5]

This dependence of the electron-mediation ability upon the structure of the organic group linking the electron donor and acceptor sites is strikingly similar to that observed for some intramolecular systems in homogeneous solution.[6] A number of inner-sphere reactions of carboxylato-cobalt(III) with Cr(II) and other aquo cation reductants also display a strong sensitivity to the structure of bound substituents that are *pendant* to the reacting redox centers as well as those that *bridge* directly these metal

ions.[7,8] The precursor complexes for these reactions, that typically

involve binding of the reductant to the carbonyl oxygen, are insufficiently

stable to enable k_{et} to be evaluated for these reactions, the observed

(second-order) rate constants for the overall reaction, k_{ob}, being determined

instead. It is therefore not known to what extent the observed carboxylate

ligand effects upon k_{ob} arise from variations in k_{et} rather than to differences

in the stability constant of the precursor state, K_p.[7]

The present communication contains unimolecular kinetic and reactant

adsorption data for the electroreduction of pentaamminecobalt(III) at mercury

and gold electrodes bridged by thiocarboxylate ligands of the form

$R-SCH_2COO^-$, where R is an alkyl, ketone, carboxylate, or aromatic substituent.

Second-order rate constants, k_h, for their outer-sphere homogeneous reduction

by $Ru(NH_3)_6^{2+}$ are also presented for comparison. Since the sulfur atom

unquestionably provides the surface binding group responsible for the very

strong adsorption of the Co(III) complexes,[2,3] R is anticipated to be a pendant,

rather than a direct bridging, group in each case. The sensitivity of the

reduction kinetics upon the structure of R is contrasted with that for

structurally related reactions where the organic substituent directly

bridges the surface donor and Co(III) acceptor sites.

Experimental

Most experimental details are available in ref. 1. The various Co(III)

complexes were prepared from the thiocarboxylate ligands (Aldrich Co.) and

aquopentaamminecobalt(III) by heating together in aqueous media.[1] The

values of k_{et} as a function of electrode potential, described in terms of

the transfer coefficient α_{et} [$= -(RT/F)(d\ln k_{et}/dE)$], were determined by using

rapid linear sweep voltammetry.[1,9] The rate constants and transfer coefficients

for the overall reaction, k_{ob} and α_{ob}, respectively, were obtained by using normal pulse polarography.[1] All electrode potentials are quoted versus the saturated calomel electrode (s.c.e.), and all measurements were made to $24 \pm 0.5°C$.

Results and Discussion

Table I summarizes electrochemical rate parameters for the reduction of eight $Co^{III}(NH_3)_5L$ complexes, where the carboxylate ligand L has the general structure $R-SCH_2COO^-$, at -200 mV at mercury and gold electrodes. The carboxylate group is bound to Co(III) in each case. Besides the unimolecular rate constants, k_{et}, for reduction of the surface-attached reactant, the corresponding rate constants for the overall reaction, k_{ob} (cm sec^{-1}), are also listed along with estimates of the precursor stability constants K_p.

The last quantity is obtained in two ways. The first method, yielding the values labelled K_p' in Table I, involves the direct measurement of Γ_p from the coulombic charge contained under the rapid linear sweep voltammetric waves employed to measure k_{et}.[1] The values of K_p' are then obtained from $K_p' = \Gamma_p/C_b$, where the bulk reactant concentration was about 50 $\mu\underline{M}$ in the present experiments. Since a monolayer corresponds to $\Gamma_p \sim 1 \times 10^{-10}$ mol cm^{-2} for the present systems, the values of K_p' around 2×10^{-3} cm in Table I correspond to a saturated adsorbate layer. The K_p' values all refer to 200 mV vs sce since this is the initial potential chosen for the rapid linear sweep voltammetry. The second method of obtaining K_p involves estimating it from the corresponding values of k_{et} and k_{ob} by using the preequilibrium expression[1,9,10]

$$K_p^{est} = k_{ob}/k_{et} \qquad (1)$$

The resulting "estimated" values, k_p^{est}, given in Table I therefore refer

to the same potential as for k_{et} and k_{ob}, -200 mV.

Most rate and adsorption parameters at mercury electrodes were

essentially independent of pH in the range ca. 2.5-7, although significant

(ca. twofold) variations in k_{et} were found for some systems (e.g., for

$R=CH_2COO^-$) containing sites that are readily protonated. In these cases,

the k_{et} values given in Table I are those obtained in neutral 0.1 $\underline{M}$ $NaClO_4$.

Acidic media needed to be employed for the kinetic measurements at gold

electrodes in order to avoid precipitation of the Co(II) product as a

hydroxide on the solid metal surface.

Inspection of Table I reveals that only small or moderate ($\leq$ fourfold)

variations in k_{et} for the reduction of $Co^{III}(NH_3)_5OOCCH_2SR$ arise from

alteration of the pendant R group. It is nonetheless worthwhile to examine

these rate variations in comparison with those for related reactions.

The rates might be expected to correlate

with the electron-withdrawing (or donating) properties of the substituent,

as measured by the Taft inductive parameter $\sigma*$,[11] since this might be

expected to influence the surface binding via variations in the electron

density of the sulfur atom and also in the thermodynamics of the Co(III)/(II)

redox couple. Although the $\sigma*$ values for the present systems are incomplete,

the rate constants for *outer-sphere* reduction by $Ru(NH_3)_6^{2+}$, k_h, do increase

consistently with increasing $\sigma*$ of the R substituent (Table I). This trend,

although only mild, is expected since the presence of electron-withdrawing

substitutents should destabilize the Co(III) reactant relative to the

Co(II) product on thermodynamic grounds. [In other words, the (unknown)

standard potential for the Co(III)/(II) redox couple will be shifted to

more positive values.] Similar, although more marked, effects are seen for

outer-sphere Co(III) reduction at electrodes as well as by $Ru(NH_3)_6^{2+}$ when

the organic substituents are bound directly to the carboxylate group.[12] By contrast, slightly *smaller* values of k_{et} are found with functional groups having larger values of $\sigma*$ (Table I). This is somewhat surprising since the substituent influence upon the cobalt redox thermodynamics might be expected to be comparable for inner- and outer-sphere redox processes.

Roughly similar variations in k_{et} are seen at gold as for those at mercury electrodes, although corresponding values differ typically by two- to three-fold. (Similar rate differences between mercury and gold have also been seen for other sulfur-attached Co(III) reactants and attributed to their differing influences upon the thermodynamics of the electron-transfer step.[1]) Marginally different transfer coefficients, α_{et}, are found for these different reactions, so that slightly differing relative values of k_{et} are obtained if a common potential other than -200 mV is selected. This potential was chosen, however, so to eliminate data extrapolation. Neither K_p^{est} nor K_p' values are listed for reactions at gold. This is because a mololayer (ca. 1×10^{-10} mol cm^{-2}) is obtained for each reactant at this surface.

Given that electron-withdrawing groups bound to the sulfur atom are expected to weaken the surface-sulfur bond, one might expect that K_p would tend to decrease as $\sigma*$ increases. However, a straightforward correlation of $\sigma*$ with neither K_p^{est} nor K_p' is evident, especially strong adsorption being obtained even with the powerful electron-withdrawing substituent R= -COCH$_3$ (Table I). Most likely these K_p values reflect the occurrence of specific interactions of all or part of R with the metal surface, although the influence of R upon adsorbate-adsorbate interactions may also be a factor. [The differences seen between corresponding values of K_p^{est} and K_p' are not unexpected given the different conditions (reactant concentrations, electrode potentials) at which they are measured.]

An interesting feature of the present results is the insensitivity of k_{et} to the extent of bond conjugation in the pendant substituent. For example,

the k_{et} values at mercury and gold for R = C_2H_5 are essentially identical to those for R = $CH_2C_6H_5$, and slightly larger than for R = C_6H_5. In contrast, replacement of the methylene linking the sulfur and carboxylate groups (system 1, Table I) by a benzene ring (system 10) yields a tenfold increase in k_{et} at mercury and a 30 fold decrease in k_{et} at gold. Part of the increase in k_{et} at mercury can be attributed to thermodynamic effects at the cobalt redox center caused by the electron-withdrawing benzene ring, as evidenced by the threefold larger value of k_h obtained under these conditions. Even though the benzene bridging group (system 10) does not provide complete double-bond conjugation between the surface and cobalt reaction centers, by inference with the behavior of related systems the enhanced reactivity of this system may well be due to greater electronic coupling; that is, associated with larger values of the electronic transmission coefficient κ_{el}.[1,2] It is likely that $\kappa_{el} \lesssim 0.1$ (i.e., decidedly nonadiabatic pathways are followed) with bridging groups having interrupted conjugation arising from the interposition of one or more methylene linkages.[1-3] Evidence for such nonadiabatic pathways for these reactions is derived in part from the unimolecular frequency factors derived from electrochemical activation parameters.[1,3,5]

The markedly smaller k_{et} value obtained with the benzene-containing bridge (system 10) at gold, however, casts doubt on the ability of this group to enhance κ_{el} and hence k_{et} via electronic transmission through the ring. A clear difference between these systems at gold and mercury electrodes is that the former surface yields uniformly close-packed reactant monolayers, while the submonolayer adsorption ($\Gamma_p \leq 2 \times 10^{-11}$ mol cm^{-2}) is encountered at mercury under the experimental conditions employed for the k_{et} measurements. Under the latter circumstances the bridging benzene group may be able to lie flat (or possibly edgewise) on the mercury surface,

enabling the Co(III) reacting center to approach more closely to the electrode. One can envisage k_{et} to be increased via enhancement of κ_{el} in this manner, electron tunneling possibly occurring via direct "through space" overlap of the metal surface and cobalt orbitals[14] as well as via the benzene ring, the $-SCH_2-$ linkage thereby being bypassed (cf. the discussion for analogous homogeneous redox systems in ref. 6a). At gold electrodes, on the other hand, the close-packed adsorbate structure presumably prevents the benzene ring from interacting specifically with the metal surface, thereby precluding the above mechanism, the smaller k_{et} value perhaps reflecting a smaller κ_{el} associated with a *larger* electrode-cobalt distance brought about by the benzene bridge. Indeed, a striking sensitivity of k_{et} to the anticipated surface-cobalt separation has been observed for the reduction of closely related thiocarboxylate adsorbates at gold.[2]

The virtual absence of such effects when benzene or other unsaturated substituents are pendant to, rather than bridging directly, the redox center and the metal surface suggests that pendant groups do not noticeably influence the degree of electronic coupling, either by altering the spatial position of the redox center or its interaction with the metal surface. Such substituents may nonetheless affect the kinetics of the overall reaction as measured by k_{ob} as a consequence of their influence upon the precursor stability K_p. Although the adsorbate-surface interactions that determine K_p may also influence the energetics of the electron-transfer step, this effect upon k_{et} will vanish if these interactions remain unchanged in the adsorbed "successor state" that follows electron transfer.[1,9] Nevertheless, small differences between the stability of the precursor and successor states that are sensitive to the particular pendant substituent may be responsible for at least part of the minor variations seen in k_{et} in Table I.

Since only moderate ($\leq$ tenfold) variations in K_p^{est} at mercury electrodes are incurred by alteration of R and these tend to be opposite to the

corresponding variations in k_{et}, the overall rate constants k_{ob} show only a minor dependence upon the nature of the pendant substitution (Table I). This ineffectiveness of the present pendant substituents for heterogeneous electron mediation contrasts with the large (ca. 10 to 100 fold) enhancements of the overall (second-order) rate constants for inner-sphere reduction of carboxylatopentamminecobalt(III) in homogeneous solution brought about by various substituents that are pendant to the "lead-in" carbonyl oxygen.[7,8] Such catalyses seems to be associated commonly with a pathway invovling intermediate reduction of the pendant substituent, or at least with "electron sharing" between the ligand and the reductant via π interactions.[8] For example, the presence of a 4-pyridine substituent is known to strongly catalyze inner-sphere Co(III) reduction by Cr^{2+}.[8a] No such catalysis for heterogeneous electron mediation is seen, however, with the 4-pyridine substituent (system 8) in Table I. As we have noted elsewhere,[12] the impetus for such "two-step" reduction pathways for homogeneous reactions via intermediate reduction of the coordinated ligands appears to be absent for electrochemical processes. This is because electrochemical reduction involves activation of one redox center, whereas a pair of reactants need to be activated simultaneously for reactions in homogeneous solution. For the latter process, therefore, any mechanism, such as intermediate ligand reduction, that enables the oxidant and reductant to be activated separately would tend to involve a smaller overall activation energy and therefore be favored over the single-step process provided that the ligand reorganization energy is suitably small. Given that the "reductant" in the electrochemical case is the electrode which clearly requires no activation anyway, such mechanisms would seem not to offer any energetic advantage over single-step electroreduction.[12]

The observed insensitivity of k_{ob} as well as k_{et} for electroreduction to the pendant group structure also contrasts with the very large (up to ca. 10^4 fold) rate enhancements seen for ostensibly outer-sphere reductions of $Co^{III}(NH_3)_5L$ reductions at mercury and gold when the carboxylate ligand L contains an alicyclic or aromatic ring.[12] These effects are due predominantly to increases in the precursor state stability (i.e., in K_p) associated with specific surface-ligand interactions.[12] The key difference between the systems in ref. 12 and those considered here is that the precursor stability for the latter is determined predominantly by the lead-in sulfur atom. Therefore surface interactions involving other functional groups on the thioorganic ligand can only exert significant influences upon the overall kinetics via alterations in k_{et}; that is, in the energetics of surmounting (or the efficiency of electron tunneling within) the transition state for the elementary electron-transfer step. At least for the present class of reactants, such an influence would appear to require the organic substituent to be directly bridging the redox center to the metal surface.
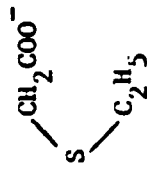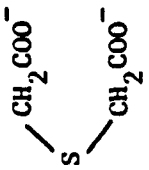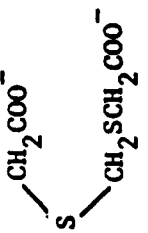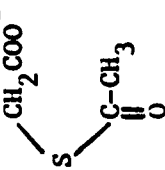
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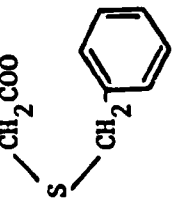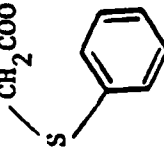
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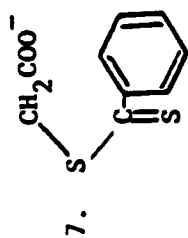3. T. T-T. Li, M. J. Weaver, Inorg. Chem., submitted.

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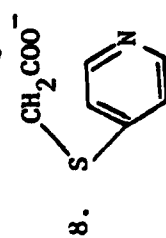12. T. T-T. Li, M. J. Weaver, Inorg. Chem., in press.

TABLE I   Kinetic and Adsorption Data for the Reduction of $Co(NH_3)_5L^{2+}$ at Mercury and Gold Electrodes in Aqueous 0.1 $\underline{M}$ $NaClO_4$, and Rate Constants for Homogeneous Reduction by $Ru(NH_3)_6^{2+}$.

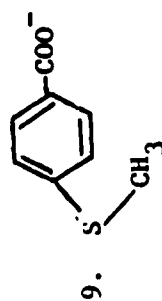| Ligand L	Surface	k_{et}^a sec^{-1}	α_{et}^b	k_{ob}^c cm sec^{-1}	α_{ob}^d	$K_p^{est\ e}$ cm	K_p^f cm	k_h^g 10^2 $\underline{M}^{-1}$ sec^{-1}	σ^{*h}
1. S(CH$_2$COO$^-$)(C$_2$H$_5$)	Hg	4.5×10^2	0.58	~0.2	0.62	$\sim4\times10^{-4}$	1.5×10^{-4}	2.2	-0.10
	Au	1.1×10^3	0.57	5×10^{-2}	0.63				
2. S(CH$_2$COO$^-$)(CH$_2$COO$^-$)	Hg	1.5×10^2	0.73	5×10^{-2}	0.62	3.5×10^{-4}	3×10^{-4}	5.0	+1.05
	Au	8×10^2	0.55	3.0×10^{-2}	0.65				
3. S(CH$_2$COO$^-$)(CH$_2$SCH$_2$COO$^-$)	Hg	5.1×10^2	0.56	4.2×10^{-2}	0.51	8×10^{-5}	5×10^{-4}	3.9	
	Au	2.5×10^2	0.60	2.5×10^{-3}	0.50				
4. S(CH$_2$COO$^-$)(C(=O)CH$_3$)	Hg	2.0×10^2	0.65	0.25	0.75	1×10^{-3}	2×10^{-3}	5.3	+1.65
	Au	4×10^2	0.67	1.3×10^{-2}	0.70				
5. S(CH$_2$COO$^-$)(CH$_2$C$_6$H$_5$)	Hg	4.5×10^2	0.56	0.10	0.56	2.5×10^{-4}	1.0×10^{-3}	4.1	+0.215
	Au	1.2×10^3	0.62	5.5×10^{-3}	0.56				
6. S(CH$_2$COO$^-$)(C$_6$H$_5$)	Hg	3.5×10^2	0.61	4.5×10^{-2}	0.56	1.3×10^{-4}	1.5×10^{-3}	4.7	+0.60
	Au	5.0×10^2	0.58	1.0×10^{-2}	0.57				

#	Structure	Metal							
7.	CH_2COO^- phenyl-S-CH$_2$COO$^-$	Hg	7.5×10^2	0.60	7×10^{-2}	0.50	1×10^{-4}	2×10^{-3}	4.3
		Au	3.0×10^2	0.60	1.1×10^{-2}	0.65			
8.	CH_2COO^- pyridyl-S-CH$_2$COO$^-$	Hg	2.5×10^2	0.60	~ 0.2	0.78	$\sim 8 \times 10^{-4}$	1.2×10^{-4}	4.6
		Au	1.1×10^2	0.60	1.0×10^{-2}	0.70			
9.	COO^- phenyl-S-CH$_3$	Hg	3.5×10^3	0.52	4.0×10^{-2}	0.60	1×10^{-5}	2.5×10^{-4}	7.3
		Au	25	0.50	2.3×10^{-4}	0.59			0
10.	COO^- phenyl-S-C$_2$H$_5$	Hg	4.5×10^3	0.58	4×10^{-2}	0.62	1×10^{-5}	1.5×10^{-4}	7.4
		Au	40	0.50	5.5×10^{-4}	0.53			-0.1

Footnotes to Table I

a Unimolecular rate constant for electroreduction of surface-attached Co(III) complex at -200 mV vs sce, obtained for ca. 50 μM bulk reactant concentration using rapid linear sweep voltammetry as outlined in ref. 1. Values at Hg electrodes were determined at sufficiently low adsorbate coverages ($\Gamma_p \lesssim 5 \times 10^{-11}$ mol cm^{-2}) so that kinetics are first order in the adsorbed reactant. Values at Au electrodes refer to coverages around half a monolayer ($\Gamma_p \sim 5 \times 10^{-11}$ moles cm^{-2}) (see text).

b Transfer coefficient for unimolecular electron-transfer step, from $\alpha_{et} = -(RT/F)(d\ln k_{et}/dE)$; determined using rapid linear sweep voltammetry.[1]

c Observed rate constant (cm sec^{-1}) for overall electrode reaction at -200 mV vs sce, determined for ca. 1 m$\underline{M}$ bulk reactant concentration by using normal pulse polarography.[1,9]

d Observed transfer coefficient for overall electrode reaction, from $\alpha_{ob} = -(RT/F)(d\ln k_{ob}/dE)$; determined by using normal pulse polarography.[1,9]

e Precursor stability constant at -200 mV vs sce, estimated from corresponding values of k_{ob} and k_{et} by using Eq. (1).

f Precursor stability constant at $+200$ mV vs sce determined from rapid linear sweep voltammetry by using $K'_p = \Gamma_p/C_b$, for bulk reactant concentration, C_b, of 60 $\mu\underline{M}$ (see text and ref. 1).

g Second-order rate constant for homogeneous reduction of Co(NH$_3$)$_5$L^{2+} by Ru(NH$_3$)$_6^{2+}$ in 0.05 $\underline{M}$ sodium trifluoroacetate-trifluoroacetic acid containing 5-20 m$\underline{M}$ acid (see ref. 1 for details).

h Taft inductive parameter[11] for pendant substituent.

END

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